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University of Canterbury, New Zealand, 12 April 2005

University of Göttingen, Germany, 19 August 2005

University of Göttingen, Germany, 1 - 30 November 2005

Carnegie Mellon University, USA, 17 November 2005

Tokyo Medical and Dental University, Tokyo, 26 November 2005

National University of Ireland, Ireland, 5 December 2005

Scope of Research

Kinetic and mechanistic analyses are made for better understandings of the chemical and physicochemical reactions occurring in polymerization systems and for better routes to the synthesis of well-defined polymers. By various polymerization techniques, in particular, living polymerizations, new well-defined polymers or polymer assemblies are prepared, and their structure/properties relationships are precisely analyzed. Projects in progress include: (1) kinetics and mechanisms of living radical polymerization (LRP). (2) Synthesis of new polymeric materials by living polymerizations and their structure/properties studies. (3) Synthesis, properties, and applications of concentrated polymer brushes (CPB).

Research Activities (Year 2005)

Presentations

Surface Interactions of CPB (Invited Lecture), Tsujii Y, and 1 other presentation, 3rd KIPS-NIST Symposium on Polymer Science, Kyoto, 19 - 20 May.

5 presentations, 54th Spring Meeting, Soc. Polym. Sci., Jpn., Yokohama, 25 - 27 May.

Structure and Properties of CPB (Invited Lecture), Tsujii Y, Workshop on Organized Macromolecular Systems, Fukuoka, 29 July.

Surface-initiated LRP and CPB: Their Unique and Striking Properties (Invited Lecture), Fukuda T, and 4 other presentations, 230th ACS Fall 2005 National Meeting, Washington DC, USA, 28 Aug - 1 September.

5 presentations, 54th Autumn Meeting, Soc. Polym. Sci., Jpn., Yamagata, 20 - 22 September.

Science for New Surface -CPB- (Invited Lecture), Fukuda T, Frontier Symposium on Polymer Science, Yamagata, 20 September.

Science and Technology of CPB, Fukuda T, and 7 other presentations, Symposium on CPB, ICR, 26 November.

Surface with CPB: Their Unique and Striking Properties (Invited Lecture), Fukuda T, and 3 other presentations, Pacificchem 2005 International Chemical Congress, Honolulu, USA, 15 - 20 December.

Synthesis of Monodisperse Silica Particles Coated with Well-Defined, Concentrated Brushes by Surface-Initiated Atom Transfer Radical Polymerization

Monodisperse silica particles (SiPs) of diameter between 100 and 1500 nm were surface-modified in a mixture of ethanol/water/ammonia with a newly designed triethoxysilane having an atom transfer radical polymerization (ATRP) initiating site, (2-bromo-2-methyl)propionyloxyhexyl triethoxysilane. The surface-initiated ATRP of methyl methacrylate (MMA) mediated by a copper complex was carried out with the initiator-fixed SiPs in the presence of a “sacrificial” (free) initiator. The polymerization proceeded in a living manner in all examined cases, producing SiPs coated with well-defined PMMA of a target molecular weight up to 480 k with a graft density as high as 0.65 chains/nm². These hybrid particles had an exceptionally good dispersibility in organic solvents. Transmission electron microscopic and atomic force microscopic observations of their monolayers prepared at the air-water interface revealed that they formed an ordered 2-dimensional lattice extending throughout the monolayer (Figure 1).

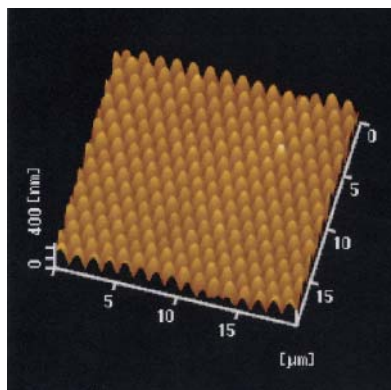


Figure 1. Ordered 2-dimensional lattice of monodisperse silica particles coated with well-defined, concentrated brushes.

Protein Repellency of Well-Defined, Concentrated Poly(2-hydroxyethyl methacrylate) Brushes by Size-Exclusion Effect

The adsorption of proteins on poly(2-hydroxyethyl methacrylate) (PHEMA) brushes was systematically studied by quartz crystal microbalance (QCM) (Figure 2) and fluorescence microscopy as a function of graft density and protein size. The graft density σ (chains/nm²) ranged from 0.007 (dilute or semi-dilute brush regime) to 0.7 (concentrated brush regime), and the protein size ranged from 2 to 13 nm in an effective diameter. The lowest-density brush ($\sigma = 0.007$) adsorbed all the tested four proteins, while the highest-density brush ($\sigma = 0.7$) adsorbed none of them. The middle-density brush ($\sigma = 0.06$) showed an intermediate behavior, adsorbing the smallest two proteins but effectively repelling the largest two. These results support the idea of size-exclusion effect, an effect characteristic of concentrated polymer brushes, in which the graft chains are highly extended and highly oriented so that large molecules, sufficiently large compared with the distance between the nearest-neighbor graft points, are *physically* excluded from the entire brush layer.

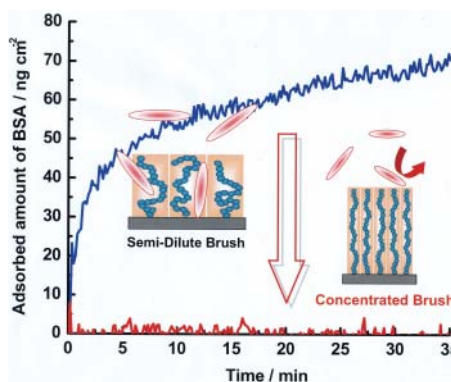


Figure 2. Adsorption of bovine serum albumin (BSA) on PHEMA brushes.

Grants

Fukuda T, Science and Technology of CPB, Grant-in-Aid for Specially Promoted Research, 1 April 2005 - 31 March 2009.

Tsujii Y, Creation of New Bio-Interfaces Based on CPB, Grant-in-Aid for Science Research (A), 1 April 2005 - 31 March 2008.

Tsujii Y, Patterning by Direct-Writing Graft Polymerization, Grant-in-Aid for Exploratory Research, 1 April 2005 - 31 March 2007.

Ohno K, Science of Semi-Soft Colloidal Crystals, Grant-in-Aid for Young Scientists (A), 1 April 2005 - 31 March 2008.

Ohno K, Fundamentals and Applications of Semi-Soft

Colloidal Crystals, Industrial Technology Research Grant Program by NEDO, 1 January 2005 - 31 December 2007.

Tanaka K, Construction of Nanoelectronic Devices, CREST, Jpn. Sci. Tech. Corp., 1 November 2002 - 31 October 2007.

Kaya K, Collaboratory on Electron Correlations, Grant-in-Aid for Cre. Sci. Res., 1 April 2001 - 31 March 2006.

Award

Tsujii Y, The Award of the Society of Fiber Science and Technology, Studies on Precise Surface Modification by LRP, The Society of Fiber Science and Technology, Japan, 8 July 2005.